

# **Nitrogen Removal From Natural Gas Using Membranes**

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## **Introduction**

According to a 1991 Energy Information Administration estimate, U.S. reserves of natural gas are about 165 trillion cubic feet (TCF). To meet the long-term demand for natural gas, new gas fields from these reserves will have to be developed. This has several important consequences.

First, low-quality fields will have to be tapped, increasing the proportion of low-quality gas in the gas supply and hence the extent of treatment required to bring the gas to pipeline specifications.<sup>1</sup> These factors highlight the need for less expensive treatment technology. Second, much of today's gas production is from large, accessible fields, whereas new production will be increasingly from small, remote or offshore fields. As a result, the need for technology suitable to treat small gas streams will increase. Third, studies performed by the Gas Research Institute (GRI Executive Summary, March, 1993)<sup>2</sup> reveal that 14% (or about 19 TCF) of known reserves in the United States are subquality due to high nitrogen content. Nitrogen-contaminated natural gas has a low Btu value and has to be upgraded by removing the nitrogen. In many cases, such reserves cannot be exploited because of the lack of suitable nitrogen-removal technology. Processes applicable to small-scale plants are particularly needed. For large scale plants, cheaper, more reliable technologies are required.

## **Objectives**

In response to the problem, the Department of Energy is seeking innovative, efficient nitrogen-removal methods. The principal processes in use are cryogenics, pressure swing adsorption (PSA) and lean oil adsorption. The cryogenic processes are the only technology used

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on any scale. Costs for cryogenic processes vary with stream composition, but are in the range \$0.30-0.50/Mscf for plants handling 75 MMscfd and increase to more than \$1.00/Mscf for plants handling 2 MMscfd or less. The other processes are more expensive and have not yet found industry acceptance.

Membrane processes have also been considered for natural gas denitrogenation. The challenge, not yet overcome, is to develop membranes with the required nitrogen/methane separation characteristics. Either glassy polymers, which are usually nitrogen-permeable, or rubbery polymers, which are usually methane-permeable, could be used. Obtaining suitable nitrogen-permeable membranes does not seem feasible. Our calculations show that a nitrogen/methane selectivity of at least 15 is required to make this type of membrane economically viable; the highest selectivity available with current polymers is only about 2-3. On the other hand, for a methane-permeable membrane to be viable, a methane/nitrogen selectivity of 4 to 6 would suffice. The objective of this project is to determine whether this target membrane selectivity can be achieved, and, if so, whether a process based on such a membrane will be technically and economically viable.

## **Approach and Technology Description**

Our approach to denitrogenation of subquality natural gas to pipeline specifications is to use methane-permeable membranes in the innovative process design shown in Figure 1. All components of the process except the membrane are completely developed and commercially available. By integrating membrane separation with a turbine expander/compressor the energy used in the membrane cooling process is minimized, and most of the high-value C<sub>3+</sub> hydrocarbons (NGL) are recovered.

The three main features of the process are:

- Use of high-performance methane-permeable membranes at low temperatures to separate the feed gas stream into a methane-rich product stream, and a nitrogen-rich waste gas stream.
- Expansion of the waste nitrogen stream in a turbo-expander/compressor assembly to cool the feed gas, while providing some of the work of compression for the purified methane stream from the membrane system.
- Recovery of the valuable C<sub>3+</sub> higher hydrocarbons (natural gas liquids) from the high-pressure feed stream by condensation, using the cooling provided by the chilled waste gas.

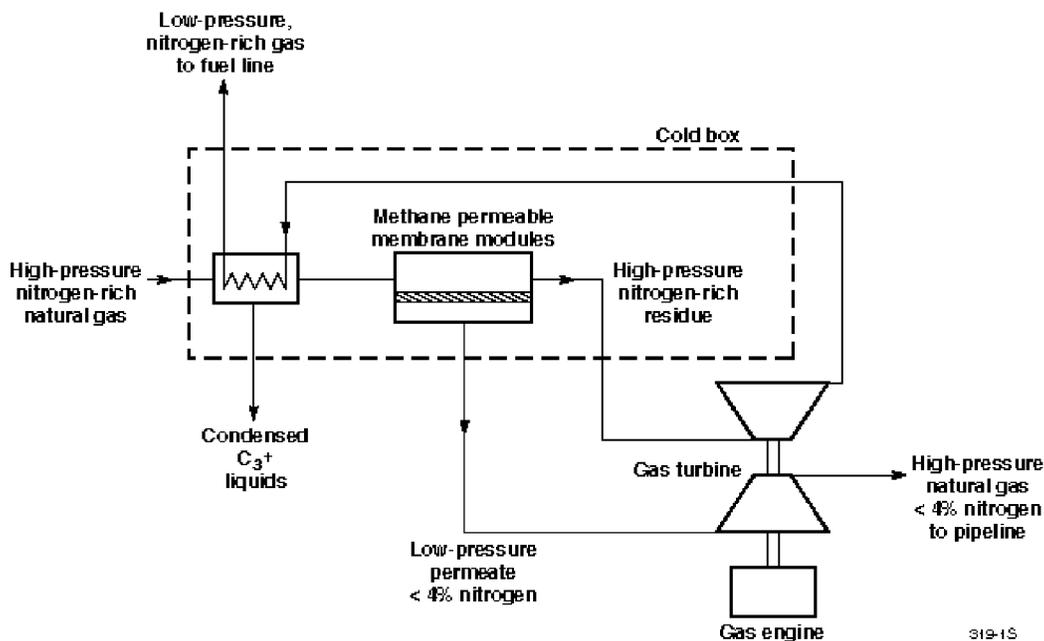


Figure 1. Simplified block diagram of a low-temperature membrane process for natural gas denitrogenation coupled with higher hydrocarbon liquid recovery.

The low-pressure nitrogen-rich gas will provide the fuel required to power the gas engine, while the condensed natural gas liquids and the high-pressure natural gas will be the revenue-producing products. More complex designs, involving integration of the membrane system with cryogenic or PSA systems, would be used for larger streams from which maximum methane recovery is desirable.

The process illustrated in Figure 1 requires methane-permeable membranes with a methane/nitrogen selectivity of 4 to 6, depending on the concentration of the nitrogen in the feed gas. The Phase I work demonstrated the feasibility of achieving such selectivities at temperatures of -20 to -50°C.

## Results

Six polymers were proposed as candidate materials: polyamide-polyether copolymer, an olefinic polymer, silicone rubber, poly(siloxylene-siloxane), poly(trimethylsilyl propyne) [PTMSP], and Teflon AF. Our preliminary evaluation of the properties of these materials showed that three of the polymers would not be viable choices for a commercial application. The olefinic polymer is likely to become too brittle on exposure to air for formation into spiral-wound modules. Poly(siloxylene-siloxane), which has promising methane/nitrogen selectivity at room temperature, is no longer commercially available. Preliminary permeation tests run with Teflon

AF showed that this polymer is selective for nitrogen over methane. We selected the remaining three, listed in Table 1, for permeation tests.

Table 1. Membrane Materials Chosen for Feasibility Study for Denitrogenation of Natural Gas. (Properties calculated from pure-gas measurements.)

Polymer Type	Methane Permeability ( $10^{-10}\text{cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ )	$\text{CH}_4/\text{N}_2$ Selectivity y at $23^\circ\text{C}$
<b>Rubbery polymers (<math>T_g &lt; -50^\circ\text{C}</math>)</b>		
Polyamide-polyether block copolymer (Pebax 2533)	20	4.2
Silicone rubber	760	3.3
<b>Superglassy polymer (<math>T_g &gt; 150^\circ\text{C}</math>)</b>		
PTMSP	17,500	2.5

The most important experimental results of the Phase I program are summarized in Table 2, which shows the effect of temperature on the separation performance of the three membranes tested.

Table 2. Summary of Permeability and Selectivity of the Three Membranes Tested in Phase I.

Membrane Type	Feed Temperature ( $^\circ\text{C}$ )	Methane Permeability Coefficient ( $10^{-10}\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ )	Membrane Selectivity (-)		
			$\text{CH}_4/\text{N}_2$	$\text{C}_3\text{H}_8/\text{CH}_4$	$\text{C}_3\text{H}_8/\text{N}_2$
Silicone Rubber	20	638	2.6	3.1	8.4
	0	461	2.9	4.1	11.9
	-35	411	4.0	7.5	30.0
Pebax 2533	22	12.5	2.8	3.0	8.4
	-35	0.175	1.6	3.2	5.1
PTMSP	20	1,716	3.0	4.2	12.6
	0	1,760	3.7	6.7	24.9
	-55	2,552	5.5	11.5	74.1

Figure 2 shows a plot of methane/nitrogen membrane selectivity obtained in a number of tests as a function of feed temperature for the PTMSP membrane. This plot shows clearly that the target methane/nitrogen selectivity of between 4 and 6 is achieved at temperatures below about  $-20^\circ\text{C}$ . Methane/nitrogen selectivities exceeding 5 were measured at temperatures below  $-50^\circ\text{C}$ .

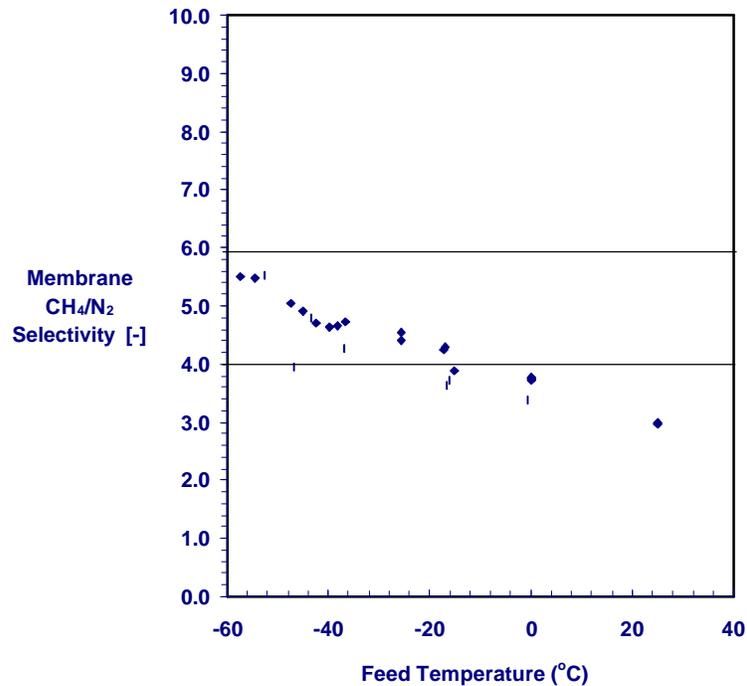


Figure 2. Methane/nitrogen selectivity as a function of feed temperature for the PTMSP membrane.

The data in Table 2 and Figure 2 show that PTMSP and silicone rubber membranes are both good candidates for the separation of nitrogen from natural gas. Both achieve the target methane/nitrogen selectivity of 4-6 at -30°C required for a viable process, and both would give even higher selectivities at lower temperatures. Based on these results, we are continuing to work with both materials in the Phase II project, making a final selection as more data become available.

## Benefits

To determine the applicability of methane-selective polymers to natural gas denitrogenation, we performed a number of process design calculations for different types of natural gas streams. A key advantage of membrane systems is that they can be designed to handle large or small gas flows and a wide range of feed concentrations. The actual membrane process design for a specific methane/nitrogen separation plant will depend on the size of the gas stream and the nitrogen content of the gas. Broadly, the application area can be divided into the following four categories:

1. Low flow rate (2-20 MMscfd)/Low nitrogen content (4-10%)
2. Low flow rate (2-20 MMscfd)/High nitrogen content (> 10%)

3. High flow rate (> 20 MMscfd)/Low nitrogen content (4-10%)
4. High flow rate (> 20 MMscfd)/High nitrogen content (> 10%)

In our economic analysis, we took as our base-case, a low-flow, low-nitrogen-content stream. We prepared a system design and analyzed the capital and operating costs for the system. A comparison with competing technologies was also made. Hybrid processes consisting of a membrane first stage followed by an adsorption, absorption or cryogenic second stage are likely to be a lower cost design for high-flow, high-nitrogen-content streams. Data from a Gas Research Institute database show that the size of the natural gas denitrogenation opportunity is large.

Of the processes being considered for nitrogen removal from natural gas (see Table 2), cryogenic distillation is the only one being used on any scale. Twelve such systems are believed to be in operation in the U.S.<sup>3</sup> Processing costs for cryogenic plants vary with stream composition and size, but are in the range \$0.20-0.33/Mscf for plants handling 75 MMscfd, and increase to more than \$1.00/Mscf for plants handling 2 MMscfd or less<sup>4</sup>. Other processes include pressure swing adsorption<sup>4</sup> and lean oil adsorption<sup>4,5</sup>. These two processes are even more expensive than cryogenic plants and have not found any significant acceptance by the industry.

Cryogenic processes are typically used to treat gas containing more than about 10% nitrogen, but the need for extensive pretreatment is a major drawback. Pretreatment generally consists of amine scrubbing to remove carbon dioxide followed by glycol dehydration to remove most of the water vapor. Molecular sieves then remove any remaining water vapor and carbon dioxide, after which the gas is cooled in a final polishing step to remove heavy hydrocarbons and aromatics. All of these components must be removed to avoid freeze-up in the cryo-section of the plant, which operates at -150°C. The gas leaving the pretreatment plant is cooled and liquefied in a series of operations involving expansion across Joule-Thompson valves, for a low-pressure product, or across expansion turbines, for a high-pressure high-quality final product. Depending on the feed conditions and the final disposition of the products, each cryogenic system is custom-designed. The complexity of the pretreatment makes operational reliability a concern. A simpler, more reliable pretreatment process would make cryogenic processes much more attractive.

In the pressure swing adsorption (PSA) process, methane and other hydrocarbons are adsorbed onto molecular sieves, leaving a nitrogen-rich gas stream<sup>4</sup>. The PSA process is most competitive, therefore, for feed streams containing a high concentration of nitrogen. Multiple beds are typically used, with complicated switching controls between beds. The capital and operating cost of these systems are relatively high. In general, PSA processes are suited to low to medium gas flows.

Lean oil absorption processes, such as the Mehra process,<sup>5</sup> have been under development for about 10 years. These processes use chilled oil to absorb methane and other hydrocarbons. The oil is then heated and flashed at lower pressure in a series of vessels, and the liberated hydrocarbon gases are collected and recompressed to pipeline pressures. High recovery of

hydrocarbons is achieved, but the process is capital intensive. As with PSA, the process is best suited for throughputs of less than about 10 MMscfd with relatively high nitrogen concentrations.

Finally, an absorption process based on nitrogen-chelating chemicals has been reported recently. A solvent containing a chelating agent absorbs nitrogen from the natural gas, leaving the methane and other hydrocarbons behind. This process is the early development stage. The chelating agents are expensive and of questionable stability, problems that are likely to be exacerbated under gas field conditions.

Table 3 compares the membrane process with currently available technologies for the separation of nitrogen from natural gas containing 8% nitrogen. The lean oil adsorption technique, applicable to higher nitrogen content streams, would have a capital cost of \$2.13 million and an operating cost of \$2.37/Mscf if used on a stream containing 25% nitrogen.

Table 3. Cost Comparison for Various Technologies Currently Available for Removal of Nitrogen from Subquality Natural Gas.

Technology	8% Nitrogen	
	Total Capital Cost* (\$/Mscfd plant capacity)	Processing Cost (\$/Mscf)
Cryogenic Distillation	1,184	1.30
PSA	1,320	1.65
Membranes	277	0.30

\*Cost figures from Reference 4. The PSA and cryogenic distillation costs were interpolated from 6% and 15% nitrogen cases in this reference.

As shown in Table 3, the economics of the single-stage membrane process, based on our analysis, are likely to be extremely competitive with alternative technologies for nitrogen content of 10% or less. This is particularly true at lower feed throughputs. The membrane process cost is about one-third that of the other technologies, assuming that a methane/nitrogen selectivity of at least 5 can be achieved.

### Future Activities

We are currently performing laboratory tests with bench-scale modules at temperatures down to -50°C. A field site for testing commercial-scale modules has been located; we anticipate testing to start in 1997. As module performance data become available, we will refine the technical and economic analysis for membrane-based nitrogen removal.

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